

Structural Analysis of Combustion Models

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Abstract

Using ReactionKinetics, a *Mathematica* based package a few dozen detailed models for combustion of hydrogen, carbon monoxide and methanol are investigated. Essential structural characteristics are pulled out, and similarities and differences of the mechanisms are highlighted. These investigations can be used before or parallel with usual numerical investigations, such as pathway analysis, sensitivity analysis, parameter estimation, or simulation.

Keywords: combustion, kinetics, mathematical modeling, Mathematica, computational chemistry, graphs of reactions,

1. Introduction

In a previous paper we presented a *Mathematica* based program package called ReactionKinetics [Nagy et al., 2012] aimed at symbolic and numerical treatment of chemical reactions. The package is especially useful when the number of species and reaction steps is larger than to allow manual investigations, i.e. if one has dozens

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or even thousands of species and reaction steps. Since the publication of the previous version we made the package capable of reading CHEMKIN files by CHEMKINImport, added dozens of new functions such as e.g.

- CHEMKINExport,
- MaxFHJWeaklyConnectedComponents,
- MinFHJWeaklyConnectedComponents,
- MaxFHJStronglyConnectedComponents,
- MinFHJStronglyConnectedComponents,
- FilterReactions,

and made the package compatible with Version 9 of *Mathematica*.

In the present paper we investigate three classes of reactions important both from the theoretical and practical points of view in combustion: models of combustion of hydrogen, carbon monoxide and methanol, respectively.

The reaction steps of hydrogen and carbon monoxide combustion form a central part of the high temperature combustion of all hydrocarbons and oxygenates. Also, hydrogen is an important fuel itself in areas like carbon-free economy, safety issues, and rocket propulsion. In the recent years, there has been an increased interest in studying the combustion of fuel mixtures consisting of carbon monoxide and hydrogen, referred to as "wet CO" or syngas. These fuels can be produced from coal and biomass via gasification, and are considered to be a promising option towards cleaner combustion technologies for power generation. Oxygenated organic compounds have been proposed as alternative fuels in order to improve the fuel properties and reduce particulates and NO_x emissions. Methanol is one of the most important oxygenated additives since it is the simplest alcohol, has high oxygen content and no C-C bonds.

The approach we use is absolutely structural in the sense that none of results depend on the values of the rate coefficients (cf. the paper Beck [1970]). We might say that we are going to discover possibilities instead of quantitatively dealing with individual

mechanisms. To put it another way, we are going to raise questions to be answered by the chemist, rather than to answer them.

The structure of our paper is as follows. Section 2 presents the necessary theoretical background and describes the models to be investigated. Section 3 shows the results.

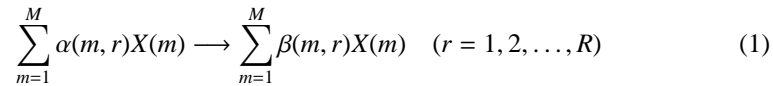
Finally, two electronic supplements are added. First, a *Mathematica* notebook showing all the details of the calculations which may be really useful for those interested in combustion modeling but annoying for the general audience. Some of the resulting figures are also given there. The reader can only redo the calculations if (s)he downloads the package itself. from here <http://www.math.bme.hu/~jtoth/CES2013>. The date can either be collected from the original authors, or from our database to be built in the near future. Second, we also attach the (very long) PDF version of our notebook which allows to passively follow what we have done, but this version does not need the *Mathematica* program. (Although the reader can download the program CDFPlayer freely, the CDF version of our notebook would not be useful in this case because of the heavy use of external data.)

2. Fundamentals for Formal Kinetics and Combustion

The basic notions can be found in textbooks such as Érdi & Tóth [1989]; Feinberg [1987, 1988]; Volpert & Hudyaev [1985]; Marin & Yablonski [2011] etc.

2.1. Feinberg–Horn–Jackson graphs, Volpert graphs, Volpert indices of reactions

Let us consider the reaction



with $M \in \mathbb{N}$ **chemical species**: $X(1), X(2), \dots, X(M)$; $R \in \mathbb{N}$ **reaction steps**,

$$\alpha(m, r), \beta(m, r) \in \mathbb{N}_0 \quad (m = 1, 2, \dots, M; r = 1, 2, \dots, R)$$

stoichiometric coefficients or **molecularities**, and suppose its deterministic model

$$\dot{c}_m(t) = f_m(\mathbf{c}(t)) := \sum_{r=1}^R (\beta(m, r) - \alpha(m, r)) w_r(\mathbf{c}(t)) \quad (2)$$

$$c_m(0) = c_m^0 \in \mathbb{R}_0^+ \quad (m = 1, 2, \dots, M) \quad (3)$$

—describing the time evolution of the concentration vs. time functions $t \mapsto c_m(t) := [X(m)](t)$ of the species—is based on **mass action type kinetics**:

$$w_r(\bar{c}) := k_r \bar{c}^{\alpha(.,r)} := k_r \prod_{p=1}^M \bar{c}_p^{\alpha(p,r)} (r = 1, 2, \dots, R).$$

((2) is also called the **induced kinetic differential equation** of the reaction (1).—Most of the statements does not utilize the special mass action form of the kinetics.) The number of **complexes** N is the number of different **complex vectors** among $\alpha(., r)$ and $\beta(., r)$, i.e. formally it is the cardinality of the set

$$\{\alpha(., r); r = 1, 2, \dots, R\} \cup \{\beta(., r); r = 1, 2, \dots, R\}.$$

The **Feinberg–Horn–Jackson graph** (or, FHJ-graph, for short) of the reaction is obtained if one writes down all the complex vectors (or simply the **complexes**, the formal linear combinations on both sides of (1)) exactly once and connects two complexes with a directed edge (or two different edges pointing into opposite directions) if the first one is transformed into the second by a reaction step. Let us denote the number of **weakly connected components** (also called **linkage classes**) of this graph by L .

The **stoichiometric space** is the linear subspace of \mathbb{R}^M generated by the **reaction vectors**: $\text{span}\{\beta(., r) - \alpha(., r); r = 1, 2, \dots, R\}$; its dimension is denoted by S . Finally, the nonnegative integer $\delta := N - L - S$ is the **deficiency** of the reaction (1). The Feinberg–Horn–Jackson graph will also be used to decide with the method proposed by Feinberg [1989] if the reaction is detailed balanced or not.

The **Volpert graph** of the reaction is a directed bipartite graph, its two vertex sets are the species set and the set of reaction steps, and an arrow is drawn from species $X(m)$ to the reaction step r if $\alpha(m, r) > 0$; (species $X(m)$ is needed to the reaction step r to take place) and an arrow goes from reaction r to species $X(m)$ if $\beta(m, r) > 0$ (species $X(m)$ is produced in the reaction step r). Sometimes it is worth labeling the edges with $\alpha(m, r)$ and $\beta(m, r)$, respectively.

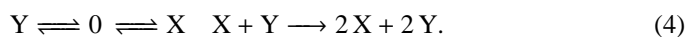
It is very useful to assign indices to the vertices of the Volpert graph. This goes in the following way. A subset of species is selected, this will be the **initial set**, (in real applications this will be the set of species with positive initial concentrations) and the elements of this set receive index zero together with all the reaction steps which

can proceed once the **initial species** are present. Next, species without an index which can be produced by the indexed reaction steps receive the index one, and reaction steps without index which can proceed receive also one, and so on.

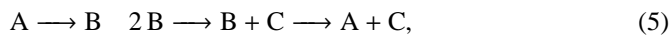
As the Volpert graph is finite, the procedure finishes in a finite number of steps. At the end either all the vertices receive an index, or some of them do not receive a finite index then one assigns index ∞ to the vertices without an index. One of the many possible interpretations of the meaning of a finite index κ is that the given species or reaction step can only appear in the κ th step or at the κ th level. In accordance with this, species with an infinite index cannot be produced, reaction steps with an infinite index cannot proceed with the prescribed initial species of the reaction. These statements and some other not less important ones can be found in a precise form e.g. in Volpert & Hudyaev [1985] or in the original paper Volpert [1972]. An application of the Volpert index in the decomposition of overall reactions is given in Kovács et al. [2004].

Simple examples from combustion theory follow to show the meaning of the definitions.

Example 1 (Mole reaction) The earliest combustion model (which has been given a detailed treatment from the point of view of the qualitative theory of differential equations) is probably the Mole reaction Mole [1936], see also Fig. 1:



Example 2 (Robertson reaction) The model proposed in Robertson [1966] contains three species, its FHJ graph is



the complexes are $A, B, 2B, B + C, A + C$, the deficiency is $N - L - S = 5 - 2 - 2 = 1$. The Volpert graph of this reaction is shown in Fig. 2.

Suppose one takes A as the only initial species, then A and the reaction step $A \longrightarrow B$ gets zero index, B and the reaction steps $2B \longrightarrow B + C$ receives 1, finally

C and the reaction step $B + C \longrightarrow A + C$ is assigned 2. (Upon selecting B one gets a similar result.) However, if one chooses C as the single initial species then all the other species and all the reaction steps will have an infinite index.

We have done all the calculations of the characteristic quantities of reactions using the package `ReactionKinetics` developed in *Mathematica* and shown also at MaCKiE 2011 [Nagy et al., 2012] and described in detail in Tóth et al. [2013]. Figures have also been drawn by the package.

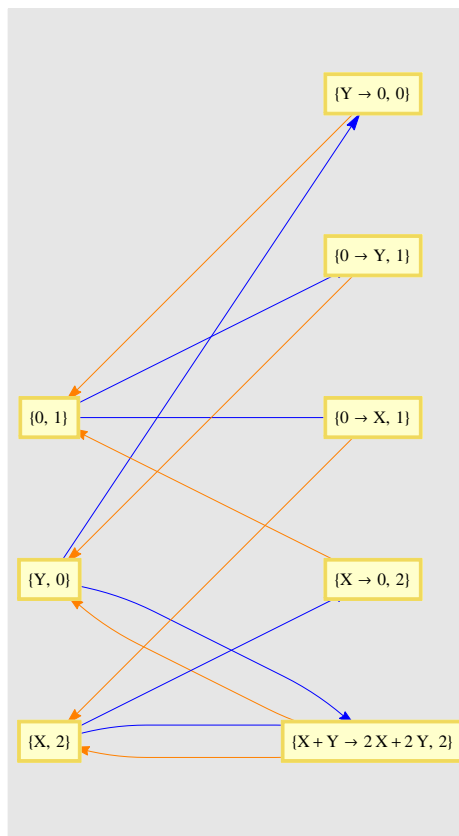


Figure 1: The Volpert graph of the Mole reaction (4)

2.2. Selected models of combustion of hydrogen, carbon monoxide and methanol

The simplest chain branching combustion reaction, the oxidation of hydrogen is already a much more complex system than the Mole and Robertson reactions discussed above. Some people feels that this system is well known and no more research is needed. However, Zsély et al. [2013] showed recently in a comprehensive mechanism comparison paper that the case is not this. The description of the experimental data is still not satisfactory and some of the recently published reaction mechanisms perform worse than older ones. Similar comparison was done by Olm et al. [2013] for the oxidation of carbon monoxide. In this work we utilize the mechanism collection of these papers, but focus on the structural differences of the mechanisms. Extending the investigation with some detailed methanol mechanisms we show that that the suggested formal mathematical handling is still applicable for even larger kinetic systems. The phenomena are more and more complex as we proceed from hydrogen through carbon monoxide to methanol. Correspondingly, the models are larger and more and more diverse.

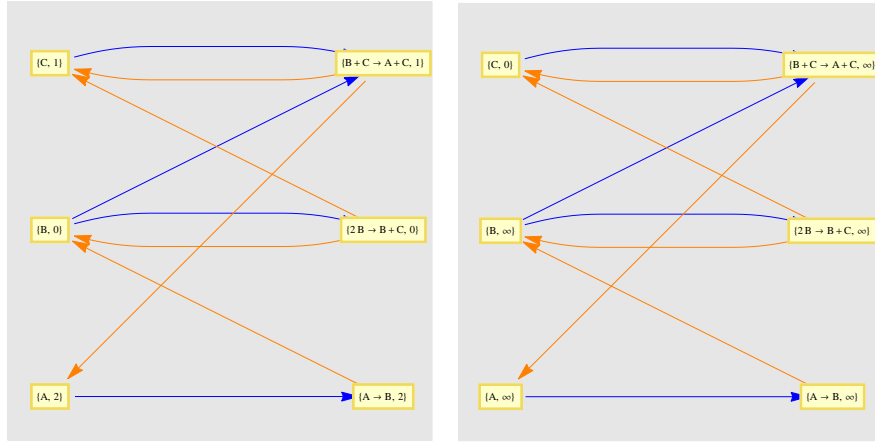


Figure 2: The Volpert graphs of the Robertson reaction (5) with B and C as initial species, respectively

3. On the structure of the selected combustion models

Even the simplest models for combustion usually contain dozens of species of reactions steps, therefore we can only show some of the results here. E.g. we do not show Volpert graphs of the investigated reactions here, because their figures are not useful, they can only be used for calculating the Volpert indices. However we have shown the Volpert graphs together with Volpert indices above for two simple reactions.

3.1. *Hydrogen*

As a starting point the basic data of the investigated mechanisms are presented in Table 1.

Table 1: Basic data of the investigated hydrogen combustion models

Mechanism	reference	M	R	$\delta = N - L - S$
Ahmed2007	Ahmed et al. [2007]	8	38	$29 - 11 - 6 = 12$
Burke2012	Burke et al. [2012]	8	38	$31 - 12 - 6 = 13$
CRECK2012	Healy et al. [2010]	8	37	$29 - 11 - 6 = 12$
Dagaut2003	Dagaut et al. [2003]	8	42	$31 - 12 - 6 = 13$
Davis2005	Davis et al. [2005]	8	40	$31 - 12 - 6 = 13$
GRI30	Smith et al.	8	40	$31 - 12 - 6 = 13$
Hong2011	Hong et al. [2011]	8	40	$31 - 12 - 6 = 13$
Keromnes2013	K��romnes et al. [2013]	9	42	$32 - 12 - 7 = 13$
Konnov2008	Konnov [2008]	8	42	$31 - 12 - 6 = 13$
Li2007	Li et al. [2007]	8	38	$31 - 12 - 6 = 13$
NUIG2010	Healy et al. [2010]	8	38	$31 - 12 - 6 = 13$
OConaire2004	�� Connaire et al. [2004]	8	38	$31 - 12 - 6 = 13$
Rasmussen2008	Rasmussen et al. [2008a]	8	40	$31 - 12 - 6 = 13$
SanDiego2011	Research [2011]	8	42	$31 - 12 - 6 = 13$
SaxenaWilliams2006	Saxena & Williams [2006]	8	42	$31 - 12 - 6 = 13$
Starik2009	Starik et al. [2010]	9	52	$41 - 16 - 7 = 18$
Sun2007	Sun et al. [2007]	8	40	$31 - 12 - 6 = 13$
USC2007	Wang et al.	8	40	$31 - 12 - 6 = 13$
Zsely2005	Zs��ly et al. [2005]	8	42	$31 - 12 - 6 = 13$

Now let us start finding the reasons why we have different numbers in different mechanisms.

Number of species, M All mechanisms contains the same, core set of species: H, H₂, H₂O, OH, H₂O₂, HO₂, O₂, O. The Keromnes2013 mechanism, formally, contains $h\nu$ as a species, but this is only a notification for the photoexcitation in a photochemical reaction. This mechanism is the only one which contains excited OH species to describe some ignition delay experiments better.

There is an other mechanism (Starik2009) which contains an additional species, the ozone. It is quite unique to include this species in a reaction mechanism

intended to be used for the description of combustion processes.

Number of reaction steps, R The number of reaction steps, R , varies between 37 and 44, except Starik2009, where this number is 52. Here, (except the mentioned case) as C. K. Law reported in his comprehensive review paper [Law, 2007] the number of reactions is approximately 5 times larger than the number of species.

Deficiency, δ The number of complexes, N , varies between 29 and 32, except Starik2009, where this number is 41. The number of weakly connected components (or linkage classes) is either 11, or 12, except again Starik2009, where this number is 16. The preliminary data suggest that Starik2009 is structurally larger or richer than the other models.

The deficiencies are large, neither the zero deficiency theorem, nor the one deficiency theory can be applied.

Weak reversibility and acyclicity None of the reactions have an acyclic Volpert graph, as all the reactions, except CRECK2012, are fully reversible. Accordingly, all the reactions are weakly reversible, except again CRECK2012, which has a single **irreversible step**: $\text{H}_2\text{O}_2 + \text{O} \longrightarrow \text{HO}_2 + \text{OH}$.

3.1.1. Representations of mechanism classes

From our—let us emphasize: structural—point of view not all the mechanisms in Table 1 are different, one has classes with exactly the same structure if the values of reaction rate coefficients are disregarded. The classes are shown in Fig. 3.

During the mechanism development one of the first steps is the decision of which species should be included in the mechanism. After this the reaction steps and the best possible (as the authors know) set of parameters are selected. This last step, the assignment of the rate parameters forms the largest part of a mechanism development work. However, we have to keep it in our mind that the parameter set corresponds to the previously fixed structure of the model. Therefore, it is important to compare the mechanisms from the point of view of their structures. This figure is a demonstrative example that the currently published hydrogen combustion mechanisms are different not at the level of the parameters, but that of their structures. It is interesting to see

that a significant number of reaction mechanisms in this collection kept the structure of the old GRI1999. It is also interesting, that when the mechanisms are updated most of the authors do not modify their structures (see the reaction mechanisms coming from the same research group, e.g. SaxenaWilliams2006 and SanDiego2011, or Li2007 and Burke2012, or OConaire2004 and NUIG2010. The structural relationship of the OConaire2004, Li2007, NUIG2010 and Burke2012 is obvious, as they are based on some older reaction mechanisms of Dryer’s group [Mueller et al., 1999].

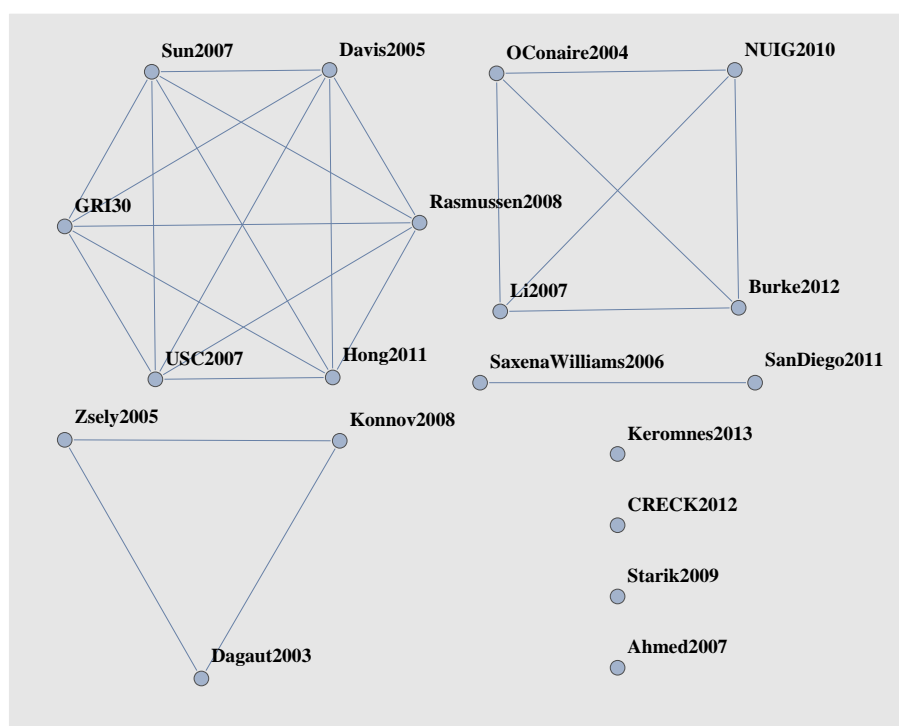


Figure 3: Classes of hydrogen combustion models. Similar models are connected with and edge of the graph.

This finding forces us to choose a single mechanism from the classes, and we remind the reader that from now on Davis2005 also represents GRI30, Hong2011, Rasmussen2008, Sun2007, USC2007; and Burke2012 also represents Li2007, NUIG2010, OConaire2004; and Dagaut2003 also represents Konnov2008, Zsely2005; and SanDiego2011

also represents SaxenaWilliams2006; whereas each of Ahmed2007, CRECK2012, Keromnes2013 and Starik2009 form a class alone. The representatives have been selected by the caprice of the alphabet.

3.1.2. Ahmed2007

As an illustration we show that Feinberg–Horn–Jackson graph in the case of the first model.

We also show the Volpert indices of the species given that the initial species are H_2 and O_2 in Table 2. (The Volpert indices of the reaction steps will only be given in the case of Burke2012 below, as an illustration.)

Table 2: Volpert indices of the species in Ahmed2007

index	species
0	O_2, H_2
1	O, HO_2, H
2	H_2O_2, OH, H_2O

One can also investigate the maximal subgraph of the Feinberg–Horn–Jackson graph. It turns out that this substructure is rather stable: The maximal subgraph of Ahmed2007, Davis2005 and SanDiego2011 and Starik2009 are the same. Also, in the case of Burke2012, CRECK2012 and Keromnes2013 we get the same subgraph. And finally, Dagaut2003 (and Konnov2008 and Zsely2005) is special, it is a kind of enlargement of the previous graphs. Chemically, OH has four different channels to be transformed as opposed to three in the other models. (Maximal can be defined either by the number of vertices or by the number of edges, in the special case of combustion models selected by us we arrive at the same subgraph using both methods.)

Let us mention that the three most important radicals in combustion (OH, O and H) form a full triangle in most of the maximal graphs except the second series: Burke2012, CRECK2012 and Keromnes2013 (including naturally the models represented by these, as well.) We shall show below one representative of each type.

3.1.3. Burke2012

The following tables show the indices of species and reaction steps if the initially present species are those with zero index.

Table 3: Volpert indices of the species in Burke2012

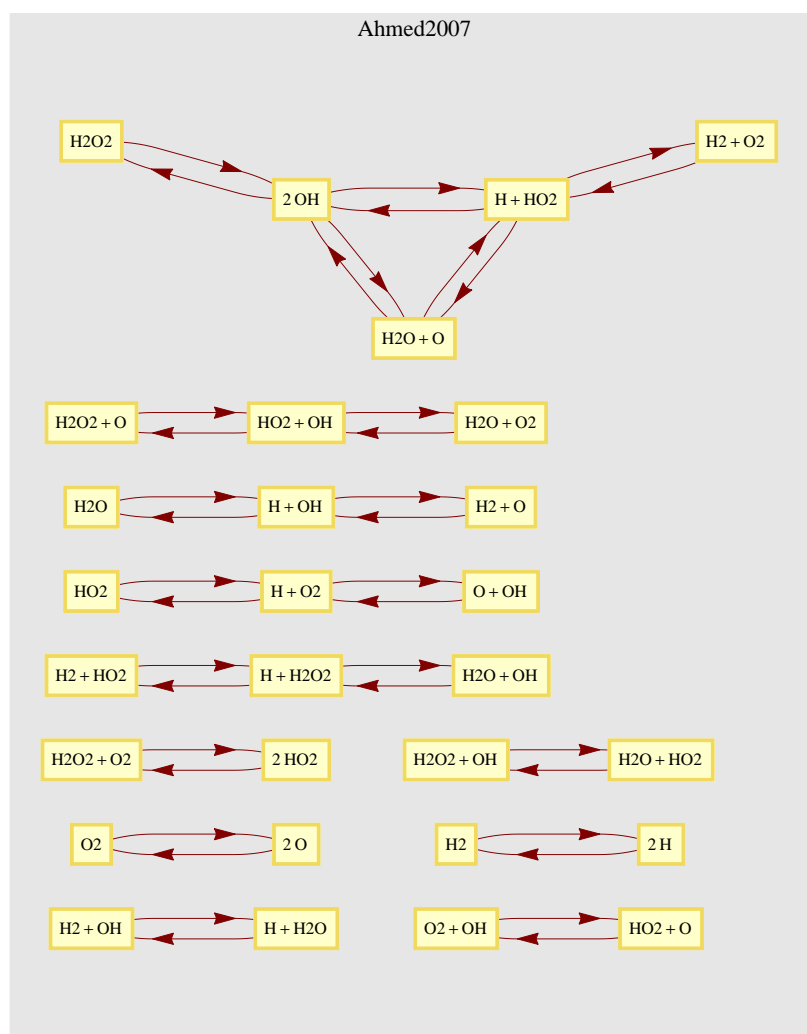


Figure 4: The FHJ graph of Ahmed2007

index	species
0	O ₂ , H ₂
1	O, HO ₂ , H
2	H ₂ O ₂ , OH
3	H ₂ O

Table 4: Volpert indices of the reaction steps in Burke2012

index	reaction steps
0	O ₂ → 2 O, H ₂ + O ₂ → H + HO ₂ , H ₂ → 2 H
1	H + O ₂ → O + OH, HO ₂ + O → O ₂ + OH, H ₂ + O → H + OH, H + O → OH, 2 O → O ₂ , H + HO ₂ → 2 OH, H + HO ₂ → H ₂ + O ₂ , 2 HO ₂ → H ₂ O ₂ + O ₂ , H + O ₂ → HO ₂ , HO ₂ → H + O ₂ , H ₂ + HO ₂ → H + H ₂ O ₂ , 2 H → H ₂
2	HO ₂ + OH → H ₂ O + O ₂ , O + OH → H + O ₂ , O ₂ + OH → HO ₂ + O, HO ₂ + OH → H ₂ O ₂ + O, H ₂ O ₂ + O → HO ₂ + OH, 2 OH → H ₂ O + O, H + OH → H ₂ + O, OH → H + O, H ₂ O ₂ + OH → H ₂ O + HO ₂ , 2 OH → H + HO ₂ , H ₂ O ₂ + O ₂ → 2 HO ₂ , H + H ₂ O ₂ → H ₂ O + OH, H + H ₂ O ₂ → H ₂ + HO ₂ , 2 OH → H ₂ O ₂ , H ₂ O ₂ → 2 OH, H ₂ + OH → H + H ₂ O, H + OH → H ₂ O
3	H ₂ O + O ₂ → HO ₂ + OH, H ₂ O + O → 2 OH, H ₂ O + HO ₂ → H ₂ O ₂ + OH, H ₂ O + OH → H + H ₂ O ₂ , H + H ₂ O → H ₂ + OH, H ₂ O → H + OH

Let us note that water only appears at the third level. This is the same with some models in other classes: CRECK2012 and Kereomnes2013; and in all the other model it appears (together with all the other species and reaction steps) earlier, at level 2.

3.1.4. CRECK2012

Table 5: Volpert indices of the species in CRECK2012

index	species
0	O ₂ , H ₂
1	O, HO ₂ , H
2	H ₂ O ₂ , OH
3	H ₂ O

CRECK2012 contains a single **irreversible step**: $\text{H}_2\text{O}_2 + \text{O} \longrightarrow \text{HO}_2 + \text{OH}$. Upon going through all the hydrogen combustion mechanisms it turns out that no other model contains any irreversible steps.

3.1.5. Dagaut2003

Here are the Volpert indices of the species given that the initial species are H₂ and O₂ in Table 6.

Table 6: Volpert indices of the species in Dagaut2003

index	species
0	O ₂ , H ₂
1	O, HO ₂ , H
2	OHEX, H ₂ O ₂ , OH
3	H ₂ O

The maximal subgraph of the Feinberg–Horn–Jackson graph of Dagaut2003 can be seen in Fig. 5.

3.1.6. Keromnes2013

Here are the Volpert indices of the species given that the initial species are H₂ and O₂ in Table 7.

Table 7: Volpert indices of the species in Keromnes2013

index	species
0	O ₂ , H ₂
1	O, HO ₂ , H
2	H ₂ O ₂ , OH, H ₂ O

The maximal subgraph of the Feinberg–Horn–Jackson graph of Starik2009 can be seen in Fig. 6.

Another interesting application can be found. Both from the point of view of thermodynamics and from the point of view of reducing the number of reaction rate coefficients one can require that a model be **detailed balance** (naturally, under the assumption that temperature and pressure are constant). Applying the pair of conditions formulated by Feinberg [1989] we get the following necessary and sufficient condition

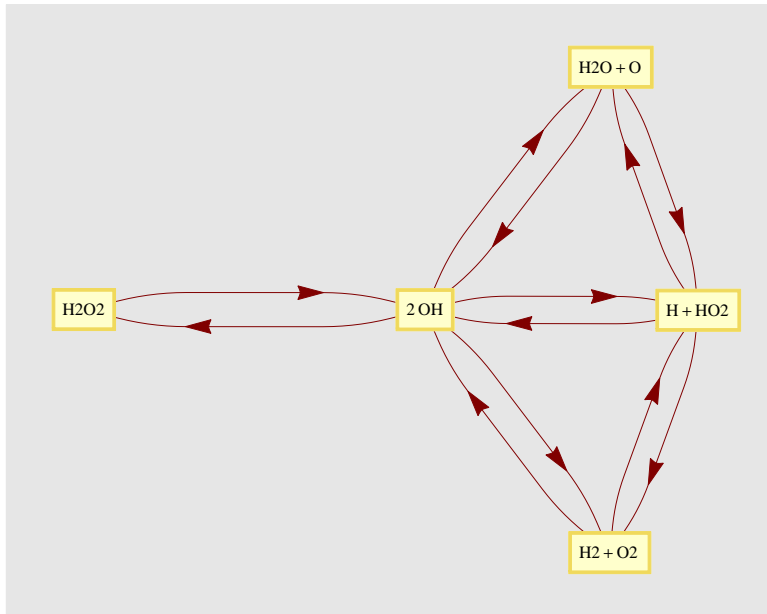
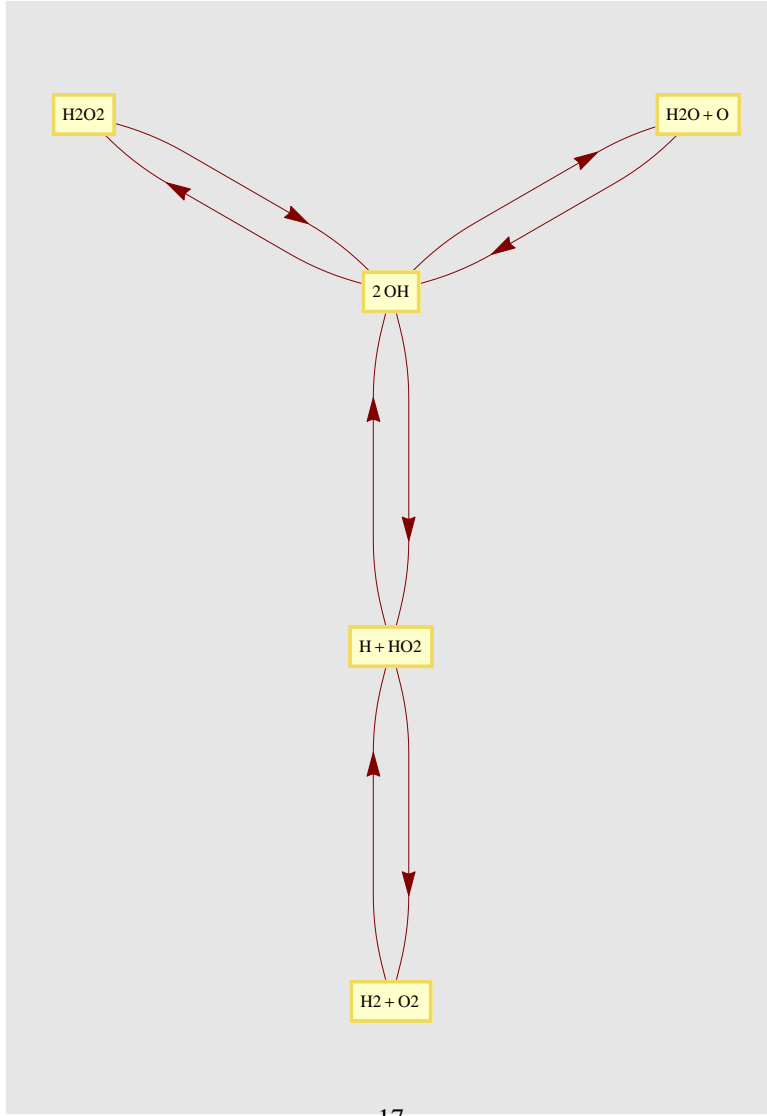


Figure 5: The maximal subgraph of the Feinberg–Horn–Jackson graph of Dagaut2003

in the case of the Keromnes2013 model (and the models represented by it):

$$\begin{aligned}
k_{26}k_{27}k_{42} &= k_{25}k_{28}k_{41}, & k_4k_{13}k_{39} &= k_3k_{14}k_{40}, & k_2k_{14}k_{17} &= k_1k_{13}k_{18}, \\
k_3k_8k_{11} &= k_4k_7k_{12}, & k_2k_4k_5 &= k_1k_3k_6, & k_2k_4k_9k_{21} &= k_1k_3k_{10}k_{22}, \\
k_2k_8k_9k_{19} &= k_1k_7k_{10}k_{20}, & k_2k_9k_{14}k_{15} &= k_1k_{10}k_{13}k_{16}, \\
k_2k_8k_9k_{13}k_{23}k_{37}^2 &= k_1k_7k_{10}k_{14}k_{24}k_{38}^2, & k_2k_8k_9k_{14}k_{24}k_{35}^2 &= k_1k_7k_{10}k_{13}k_{23}k_{36}^2, \\
k_1k_8k_{10}k_{13}k_{24}k_{33}^2 &= k_2k_7k_9k_{14}k_{23}k_{34}^2, & k_1k_8k_9k_{13}k_{24}k_{29}^2 &= k_2k_7k_{10}k_{14}k_{23}k_{30}^2, \\
k_2k_8k_9k_{13}k_{24}k_{25}^2 &= k_1k_7k_{10}k_{14}k_{23}k_{26}^2, & k_2k_4^2k_8k_9k_{13}k_{24}k_{31}^2 &= k_1k_3^2k_7k_{10}k_{14}k_{23}k_{32}^2
\end{aligned}$$



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Figure 6: The maximal subgraph of the Feinberg-Horn-Jackson graph of Keromnes2013

Further investigations may also use the extended theory by Gorban & Yablonsky [2011].

3.1.7. Starik2009

Here are the Volpert indices of the species given that the initial species are H_2 and O_2 in Table 8.

Table 8: Volpert indices of the species in Starik2009

index	species
0	O_2, H_2
1	O_3, O, HO_2, H
2	H_2O_2, OH, H_2O

The maximal subgraph of the Feinberg–Horn–Jackson graph of Starik2009 can be seen in Fig. 7.

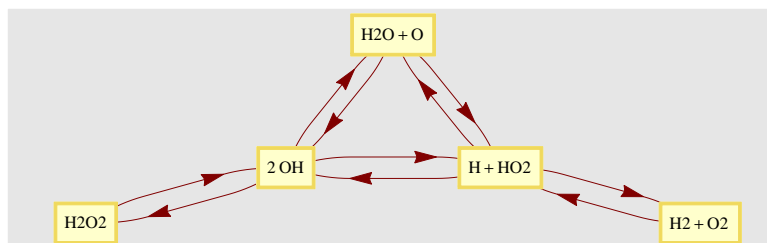


Figure 7: The maximal subgraph of the Feinberg–Horn–Jackson graph of Starik2009

3.1.8. Similarities and differences between the models of hydrogen combustion

We can further analyse the similarities and differences between the class representatives of hydrogen combustion models. One can easily determine which are the reaction steps present in one model and missing in the other. This is a very huge table, a simpler one is obtained if one only calculates the number of (irreversible, as usual) reaction steps present in one model and missing in the other.

Table 9: Number of different reaction steps in the different models

	Ahmed 2007	Burke 2012	CRECK 2012	Dagaut 2003	Davis 2005	Keromnes 2013	SanDiego 2011	Starik 2009
Ahmed2007	0	2	3	0	0	2	0	0
Burke2012	2	0	3	0	0	0	0	0
CRECK2012	2	2	0	2	2	2	0	2
Dagaut2003	4	4	7	0	2	4	2	2
Davis2005	2	2	5	0	0	2	0	0
Keromnes2013	6	4	7	4	4	0	4	4
SanDiego2011	4	4	5	2	2	4	0	2
Starik2009	14	14	17	12	12	14	12	0

Table 9 shows again that Starik2009 and Keromnes2013 contain a quite few reaction steps missing in the other models.

Let us see a single example. The reaction steps what Ahmed2007 contains but Burke2012, CRECK2012 and Keromnes2013 do not are $\text{H} + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{O}$ in all cases, and in the case of CRECK2012 $\text{H}_2\text{O}_2 + \text{O} \leftarrow \text{HO}_2 + \text{OH}$, as well. Reaction steps contained in CRECK2012 and missing in Ahmed2007 are $\text{HO}_2 \rightleftharpoons \text{O} + \text{OH}$ and $\text{H}_2\text{O}_2 + \text{O} \rightarrow \text{HO}_2 + \text{OH}$. The examples should make clear why Table9 is not symmetric.

This shows that in Table 9 reaction steps may mean either an irreversible step, or a reversible pair.

So much should suffice for those interested in the methods, those interested in real combustion chemistry should consult all the details in the supplement.

3.2. Carbon monoxide

Let us collect now the basic data of carbon monoxide combustion mechanisms into Table 10.

Table 10: Basic data of the investigated carbon monoxide combustion models

Mechanism	reference	M	R	$\delta = N - L - S$
Ahmed2007	Ahmed et al. [2007]	12	72	$57 - 23 - 9 = 25$
CRECK2012	Healy et al. [2010]	11	60	$49 - 19 - 8 = 22$
Dagaut2003	Dagaut et al. [2003]	12	68	$52 - 21 - 9 = 22$
Davis2005	Davis et al. [2005]	11	60	$47 - 19 - 8 = 20$
GRI30	Smith et al.	12	74	$57 - 23 - 9 = 25$
Keromnes2013	Kéromnes et al. [2013]	12	64	$52 - 21 - 9 = 22$
Li2007	Li et al. [2007]	12	78	$61 - 24 - 9 = 28$
NUIG2010	Healy et al. [2010]	12	78	$61 - 24 - 9 = 28$
Rasmussen2008	Rasmussen et al. [2008a]	13	88	$66 - 26 - 10 = 30$
SanDiego2011	Research [2011]	12	74	$57 - 23 - 9 = 25$
SaxenaWilliams2006	Saxena & Williams [2006]	11	60	$45 - 18 - 8 = 19$
Starik2009	Starik et al. [2010]	13	88	$70 - 28 - 10 = 32$
Sun2007	Sun et al. [2007]	12	66	$52 - 21 - 9 = 22$
USC2007	Wang et al.	12	74	$57 - 23 - 9 = 25$
Zsely2005	Zsély et al. [2005]	11	62	$47 - 19 - 8 = 20$

Since the reaction mechanism of the hydrogen oxidation is a submechanism of that of the carbon monoxide oxidation all CO mechanisms can be used for the description of the combustion of hydrogen. This means that all mechanisms in Table 8 appear in Table 1, but in the previous chapter we focused on the hydrogen submechanisms only. Although the references show a large overlap with those in Table 1, here we focus on the submechanism describing carbon monoxide combustion. Now let us start finding the reasons why we have different numbers in different mechanisms.

Species and their number, M Here one sees a much more diversified picture. The core species present in all the mechanisms are CO, CO₂, H, H₂, H₂O, HCO, HO₂, H₂O₂, O, O₂, OH. Species outside this set can be seen in Table 11.

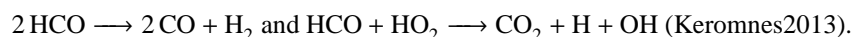
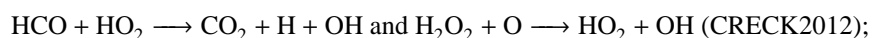
Table 11: Species present only in a given mechanism

Particular species	Mechanisms
CH ₂ O	Ahmed2007, Dagaut2003, GRI30, Li2007, NUIG2010, Rasmussen2008, SanDiego2011 Starik2009, Sun2007, USC2007
OHEX	Keromnes2013
HOCO	Rasmussen2008
O ₃	Starik2009

Number of reaction steps, R The number of reaction steps, R , varies between 60 and 88. The law of C. K. Law reported in his comprehensive review paper [Law, 2007] that the number of reactions is approximately 5 times larger than the number of species is fulfilled again.

Deficiency, δ The number of complexes, N , varies between 45 and 66. The number of weakly connected components (or linkage classes) changes between 18 and 28. The deficiencies are large, neither the zero deficiency theorem, nor the one deficiency theory can be applied.

Weak reversibility and acyclicity None of the reactions have an acyclic Volpert graph, as all the reactions, except CRECK2012 and Keromnes2013, are fully reversible. The mentioned two mechanism both contain two irreversible steps:



Although, irreversible steps are acceptable modelling tools, there are at least two problems with them. If only one way of the reaction is used the negligibility of the reverse reaction step may depend on the circumstances and it is possible that the mechanism will be used in such conditions where this simplification assumption will not be valid. In case both directions are present in a mechanism both of their values should change according to the thermodynamic equilibrium if they are re-parametrized.

3.2.1. Representations of mechanism classes

The situation is much simpler here, in the case of carbon monoxide combustion models. From the structural point of view USC2007 is identical to GRI30, NUIG2010 is identical to Li2007, and all the other mechanism are different. Therefore we do not introduce classes of mechanism here.

3.2.2. Similarities and differences between the models of carbon monoxide combustion

Table 12: Species present in one CO model and missing in others 1

Mechanism	Ahmed 2007	CRECK 2012	Dagaut 2003	Davis 2005	GRI30	Keromnes 2013	Li 2007
Ahmed2007	0	19	12	14	2	16	2
CRECK2012	7	0	6	7	7	6	6
Dagaut2003	8	14	0	8	8	8	4
Davis2005	2	7	0	0	0	2	2
GRI30	4	21	14	14	0	16	2
Keromnes2013	8	10	4	6	6	0	4
Li2007	8	24	14	20	6	18	0
Rasmussen2008	16	34	24	28	14	29	12
SanDiego2011	4	19	14	14	2	16	4
SaxenaWilliams 2006	4	7	2	2	2	4	4
Starik2009	16	35	24	28	16	29	14
Sun2007	6	12	0	6	6	6	2
Zsely2005	4	9	0	2	2	4	4

Table 13: Species present in one CO model and missing in others 2

Mechanism	Rasmussen 2008	SanDiego 2011	Saxena Williams 2006	Starik 2009	Sun 2007	Zsely 2005
Ahmed2007	0	2	16	0	12	14
CRECK2012	6	5	7	7	6	7
Dagaut2003	4	8	10	4	2	6
Davis2005	0	0	2	0	0	0
GRI30	0	2	16	2	14	14
Keromnes2013	5	6	8	5	4	6
Li2007	2	8	22	4	14	20
Rasmussen2008	0	16	30	14	24	28
SanDiego2011	2	0	14	2	14	14
SaxenaWilliams 2006	2	0	0	2	2	2
Starik2009	14	16	30	0	24	28
Sun2007	2	6	8	2	0	6
Zsely2005	2	2	4	2	2	0

As an illustration let us calculate the Volpert indices of Zsely2005 under the assumption that the species O_2 , H_2 and CO are initially present.

Table 14: Volpert indices of the species in Zsely2005

index	species
0	O_2 , H_2 , CO
1	O , HO_2 , H , OH , HCO , CO_2
2	H_2O_2 , H_2O

The maximal components of the Feinberg–Horn–Jackson graphs are the same as those found in the case of hydrogen combustion models. The reason of this is, that there are not enough carbon containing species in the models to form larger subgraphs, which is not the case with methanol models.

3.3. Methanol

Let us start again with the basic data, see Table 15.

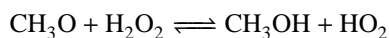
Table 15: Basic data of the investigated methanol combustion models

Mechanism	reference	M	R	$\delta = N - L - S$
Aranda2013	Aranda et al. [2013]	76	1063	$661 - 187 - 71 = 403$
Klippenstein2011	Klippenstein et al. [2011]	18	172	$122 - 42 - 15 = 65$
Li2007	Li et al. [2007]	18	170	$121 - 42 - 15 = 64$
Rasmussen2008	Rasmussen et al. [2008b]	28	320	$222 - 75 - 24 = 123$
ZabettaHuba2008	Zabetta & Hupa [2008]	58	724	$500 - 163 - 54 = 283$

The analysis of these models is much harder.

Species, classes of mechanisms The number of reaction steps is around ten times that of the species here.

There is a striking similarity of Klippenstein2011 and Li2007 at the level of numbers. Really, they use the same set of species, and the only difference between their reaction steps is that Klippenstein2011 contains also the step



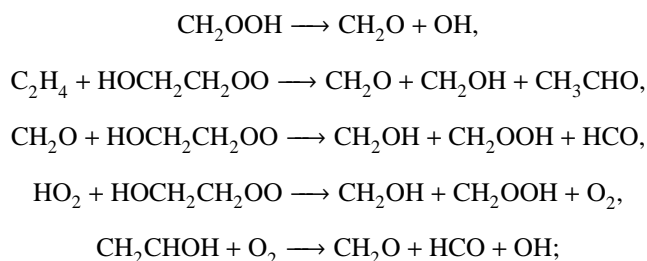
beyond the common steps. It is in accordance with the statement of the authors that they only made a small change on the structure of Li2007.

Otherwise, methanol models are so different that the question of classes and their representation does not even come up.

Number of reaction steps, R The number of reaction steps, R , ranges between 18 and 76.

Weak reversibility and acyclicity None of the reactions have an acyclic Volpert graph, as Li2007, Rasmussen2008 and ZabettaHuba2008 are fully reversible, and most of the reaction steps of the two other reactions are reversible. The exceptions are

that Aranda2013 contains the irreversible steps



whereas Rasmussen2008 contains the irreversible steps



and all the other steps in all the other mechanisms are reversible.

Deficiency, δ There is no room for the application of deficiency either. As even the smallest FHJ graph is too large to be shown here, still we shall deal with the largest subgraphs of the FHJ graph of the individual mechanisms. Volpert graphs will only be used for indexing, and will show some interesting relationships.

3.3.1. Aranda2013

The maximal weakly connected components or linkage classes of the FHJ graph of Aranda2013 are shown in Fig. 8.

Starting from CH_2O as initial species all the reaction steps can finally take place and all the species will be produced, except those steps where compounds of nitrogen occur in the reactant complex. If one takes $\{\text{CH}_2\text{O}, \text{NO}_2, \text{NH}_3\}$ as the initial set, then all the steps are capable of taking place and all the species will be produced and the largest index is now 4. Are there any species containing two carbon atoms (or C–C bonds, as these expressions are synonymous in this case)? Yes, there are more than twenty. And—beyond Aranda2013—it is only ZabettaHuba2008 where species with not less than two carbon atoms can be found, see below.

3.3.2. Klippenstein2011

The maximal weakly connected components or linkage classes of the FHJ graph of Klippenstein2011 or Li2007 are shown in Fig. 9.

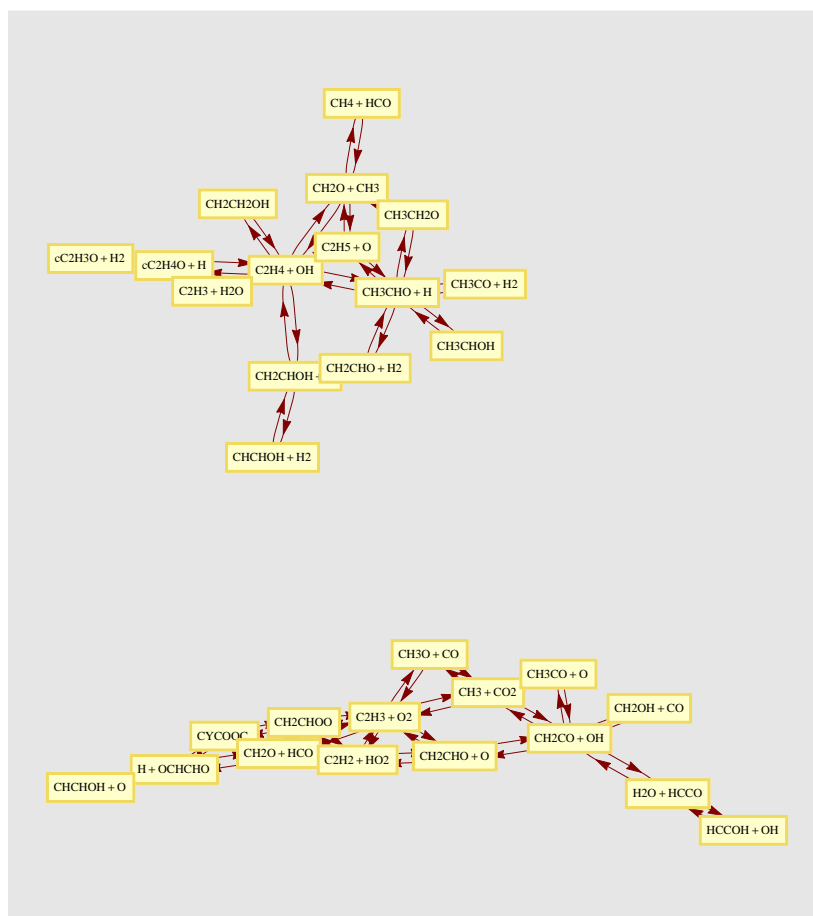


Figure 8: The maximal weakly connected components of Aranda2013

Starting from CH_2O as initial species all the reaction steps can finally take place and all the species will be produced. The species H_2O_2 and all the reaction steps where this species is a reactant species (and only those) will appear latest, only at level four.

3.3.3. Li2007

No wonder that the situation is the same as with Klippenstein2011.

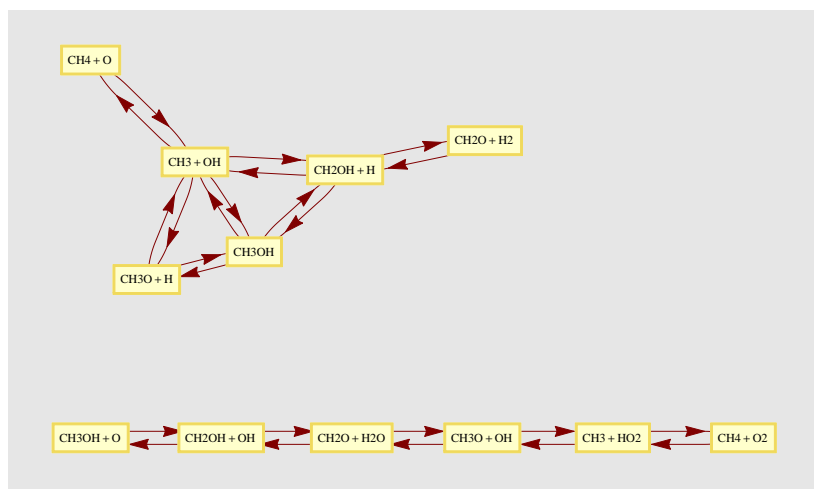


Figure 9: The maximal weakly connected components of Klippenstein2011 and Li2007

3.3.4. Rasmussen2008

The maximal weakly connected component or linkage class of the FHJ graph of Rasmussen2008 is shown in Fig. 10.

Starting from CH_2O as initial species all the reaction steps can finally take place and all the species will be produced, except those steps where compounds of nitrogen occur in the reactant complex. If one also adds NO initially, then all the steps are capable of taking place and all the species will be produced. If the set of initial species is $\{\text{CH}_2\text{O}, \text{NO}_2\}$, then the situation is even better: the largest index is now only 3.

3.3.5. ZabettaHuba2008

The maximal weakly connected component or linkage class of the FHJ graph of ZabettaHuba2008 is shown in Fig. 11.

Again, if the initial species is only CH_2O , then no nitrogen compounds (and radicals etc.) are produced. However, adding NH_3 initially, all the species and reaction steps receive a finite Volpert index.

Are there any species containing two carbon atoms? Yes, there are: CH_2CO , HCCO .

3.3.6. Similarities and differences between the models of methanol combustion

The mechanisms are too large (especially Aranda2013) to present here all the details. However, it is possible to show the number of reaction steps present in the different models and missing in the others, see Table 16.

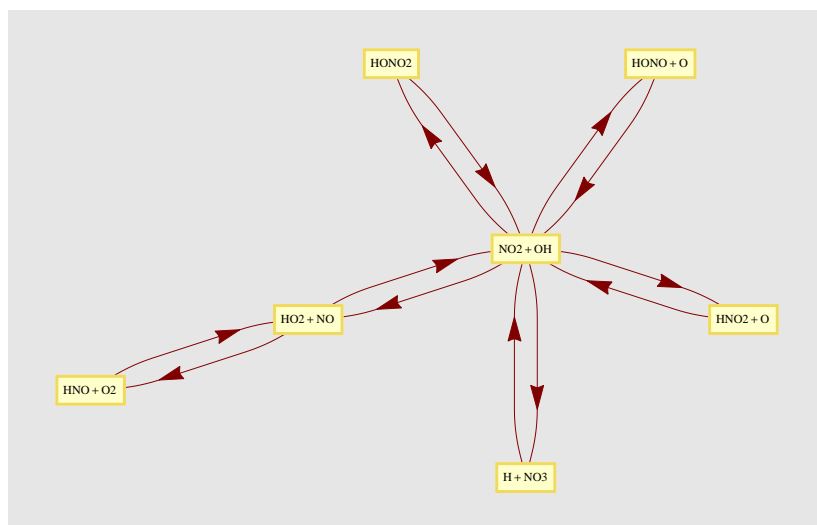


Figure 10: The maximal weakly connected component of Rasmussen2008

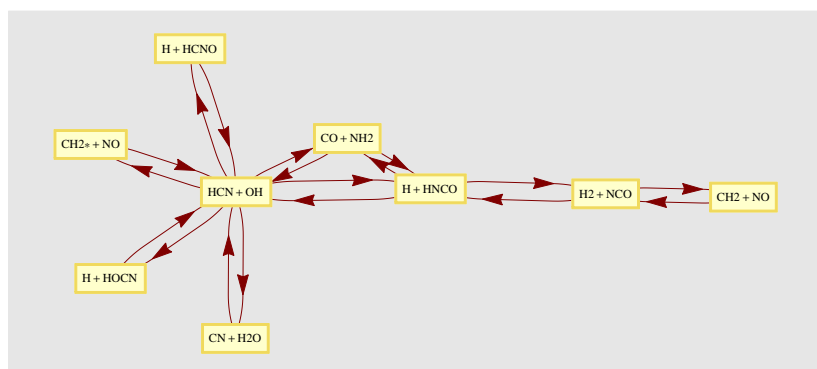


Figure 11: The maximal weakly connected component of ZabettaHuba2008

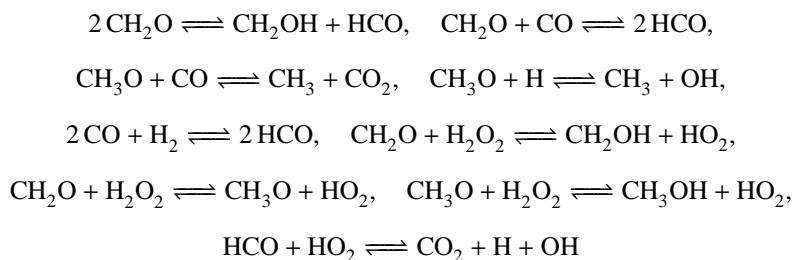
Table 16: The number of different reaction steps in the different models

	Aranda 2013	Klippenstein 2011	Li 2007	Rasmussen 2008	ZabettaHuba 2008
Aranda2013	0	897	899	759	737
Klippenstein2011	6	0	2	8	18
Li2007	6	0	0	6	16
Rasmussen2008	16	156	156	0	120
ZabettaHuba2008	398	570	570	524	0

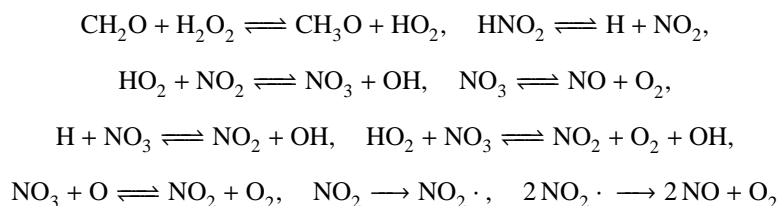
Thus, 897 in the first row, second column in Table 16 means that there are altogether 897 reaction steps enumerated in Aranda2013 but missing in Klippenstein2011. Note that the table is not symmetric, it should not be in general.

Let us see a few examples in more detail. As Li2007 is a proper subset of Klippenstein2011, there is no reaction step present in the first one and missing in the second.

The reaction steps present in Klippenstein2011 and missing in ZabettaHuba2008 are:



Finally, Rasmussen2008 contains a few reaction steps among nitrogen compounds (including two irreversible steps) which are not present in the huge Aranda2013. These are as follows.



4. Discussion and outlook

The major application of the methods outline in the paper might be that before starting quantitative analysis like estimating the reaction rate constants etc. one analyses the structure of the models at hand.

A systematic use of Volpert indexing may also serve for selecting a minimal initial set of species: the least number of species which is enough for all the reaction steps in a given model to occur and for all the species to be produced.

Another possible application is that one starts from a big model and deletes reaction routes obeying some restrictions. E.g. one starts from a CO combustion model and deletes reaction steps containing C, thus we should arrive at a hydrogen combustion model etc. The results are only useful if they are exported to a CHEMKIN file, CHEMKINExport will serve for this purpose.

We also hope that our method can and will be applied in metabolism and atmospheric chemistry research, as well.

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